CHEM1047 – Week 5 Lecture 2 – Differentials

The differential is a generalisation of the notion of small increment. In the discussion so far, we were working with finite increments (e.g. $\Delta f$ and $\Delta x$) or with limit expressions in which those increments vanished after the limit was taken. Differential expressions combine those methods: $dx$ stands for an increment of $x$ that is infinitesimally small.

1. Formal definition of the differential

In mathematics, the differential is formally defined as the limit of a small increment:

\[
\begin{align*}
 f(x + \Delta x) &= f'(x) + f''(x) \Delta x - \varphi(x, \Delta x) \Delta x \\
 f(x + \Delta x) - f(x) &= f'(x) \Delta x - \varphi(x, \Delta x) \Delta x \\
 \Delta f &= f''(x) \Delta x - \varphi(x, \Delta x) \Delta x \\
 df &= f'(x) \, dx
\end{align*}
\]

Differential expressions are more compact and convenient than the expressions involving limits of finite increments. Equation (1) also clarifies the origin of Leibniz’s notation for the derivative:

\[
df = f'(x) \, dx \quad \Rightarrow \quad \frac{df}{dx} = f'(x)
\]

Differentials will appear naturally in the construction of the definite integral where they correspond to infinitesimally small area or volume elements that the integral is adding up. The differential of a function may also be viewed as its local linear approximation.

2. Properties of differentials

The properties follow from the corresponding derivative properties. For sums and multiples:

\[
d[f + g] = df + dg, \quad d[\alpha f] = \alpha df
\]

where $\alpha$ is a constant. For products and fractions:

\[
d[fg] = fdg + gdf, \quad d\left[\frac{f}{g}\right] = \frac{fdg - gdf}{g^2}
\]

Here, $d$ is not a variable or a function, but a differential operator – an instruction to compute the differential of whatever appears in front.

Differential notation is powerful – the chain rule that has taken a page of limit expressions a few lectures ago can now be derived in one line:

\[
df = f'(g) \, dg, \quad dg = g'(x) \, dx \quad \Rightarrow \quad d\left[f\left(g(x)\right)\right] = f'(g(x))g'(x) \, dx
\]
\[ y = f(x) \quad \Rightarrow \quad \frac{dy}{dx} = f'(x) \]
\[ x = f^{-1}(y) \quad \Rightarrow \quad \frac{dx}{dy} = \left( \frac{dy}{dx} \right)^{-1} = \frac{1}{f'(x)} = \frac{1}{f'(f^{-1}(y))} \quad (6) \]

**Example 1:** calculate the differential of \( \exp(-x^2/2) \).

**Solution:** from the definition in Equation (2)
\[ d \left[ \exp(-x^2/2) \right] = \exp(-x^2/2) d \left( -x^2/2 \right) = -x \exp(-x^2/2) dx \]

**Example 2:** if \( \frac{df}{dx} = \cos x \) and \( x = t^3 \), derive the expression for \( \frac{df}{dt} \).

**Solution:** we can calculate \( dx \) and replace it
\[ dx = 3t^2 dt \quad \Rightarrow \quad \frac{df}{dx} = \frac{df}{3t^2 dt} = \cos(t^3) \quad \Rightarrow \quad \frac{df}{dt} = 3t^2 \cos(t^3) \]

**Example 3:** given that \( y = a \sin x \), calculate \( dx/dy \).

**Solution:** we can use the fact that \( dx/dy \) can be interpreted as a ratio of the two differentials
\[ y = a \sin(x) \quad \Rightarrow \quad \frac{dy}{dx} = a \cos(x) \quad \Rightarrow \quad \frac{dx}{dy} = \frac{1}{a \cos(x)} \]
\[ \frac{dx}{dy} = \frac{1}{a \sqrt{1 - \sin^2(x)}} = \frac{1}{a \sqrt{1 - y^2/a^2}} = \frac{1}{\sqrt{a^2 - y^2}} \]

### 3. Differentials of multivariate functions

Multivariate functions change value if any of their arguments changes. The expression for the differential of a multivariate function therefore is:
\[ df(x, y, z, ...) = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz + ... \quad (7) \]

A subtle point here is that not every expression of the form
\[ [...] dx + [...] dy + [...] dz + ... \quad (8) \]

is a differential of a well-behaved function because mixed second derivatives must be equal, e.g.:
\[ \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (9) \]

A differential that satisfies this property is called an exact differential. Such differentials are important in thermodynamics because their integrals are path-independent. To find out if a particular expression is an exact differential, one must compare mixed second derivatives, for example:
Here, $g(x, y)$ and $h(x, y)$ are already first partial derivatives of something – see Equation (7) – and therefore only one further derivative, with respect to the other variable, needs to be calculated.

Mixed derivative relations are useful in thermodynamics. Consider the full differential of enthalpy:

$$ H = U + PV \quad dH = dU + PdV + VdP $$

From the second law of thermodynamics $dU = TdS - PdV$, and therefore

$$ dH = TdS + VdP $$

For this to be an exact differential, we must have:

$$ \frac{\partial T(P, S)}{\partial P} = \frac{\partial V(P, S)}{\partial S} $$

Such relations are called Maxwell’s relations.

**Example 4:** calculate the differential of $f(x, y) = x \sin y$.

**Solution:** from the definition

$$ df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = \frac{\partial}{\partial x} (x \sin y) dx + \frac{\partial}{\partial y} (x \sin y) dy = \sin(y) dx + x \cos(y) dy $$

**Example 5:** find out if $(x^2 - y^2) dx + 2xydy$ is an exact differential.

**Solution:** calculating mixed derivatives yields

$$ \frac{\partial}{\partial y} (x^2 - y^2) = -2y \quad \frac{\partial}{\partial x} (2xy) = 2y $$

The derivatives are not equal, and therefore the differential is not exact.